Communications

Synthesis, Structure, and Dynamic Properties of a Fulvalene-Bound Fischer-Type Carbene Complex. A Novel Thermal Elimination of Propene†

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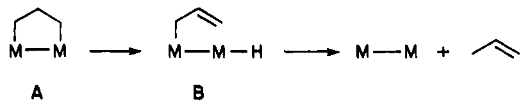
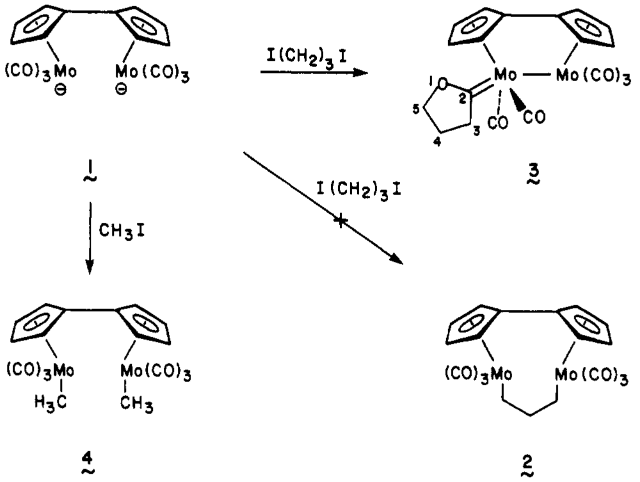
Summary: (η^5:η^5-Fulvalene)hexacarbonyldimolybdenum dianion (**1**) undergoes dialkylation with 1,3-diiodopropane to furnish the structurally characterized, metal–metal bonded 1-oxacyclapent-2-ylidene **3**, the first Fischer-type carbene to exhibit fluxional behavior, presumably through a bridging carbene species ($\Delta G^\ddagger$ = 18 ± 0.5 kcal mol^{-1}) Thermal and photochemical degradation leads to the efficient generation of propene and (η^5:η^5-$C_{10}H_8$)$(CO)_6Mo_2$ by a novel pathway not involving metallacycle **2**.

Dimetallacyclopentane moieties A (Scheme I) incorporated in soluble transition-metal complexes have been implicated as possible intermediates in propene formation from methylene fragments and ethylene[1] and as homogeneous models for surface reactions such as Fischer–Tropsch synthesis.[2] β-Hydride transfer to B followed by (binuclear?) elimination are formulated as (or tacitly assumed to be) the crucial steps in the extrusion of propene from A. We report the synthesis of a fulvalene-bridged 1-oxacyclopent-2-ylidene 3 that also thermally degrades to propene *but clearly not via a dimetallacyclic pathway.* Our work points out that other mechanisms than the one suggested have to be considered as possible routes to propenes from A. Complex 3 is also the first Fischer-type carbene to exhibit fluxional behavior, a property possibly related to its unique reactivity.

Scheme I



Scheme II



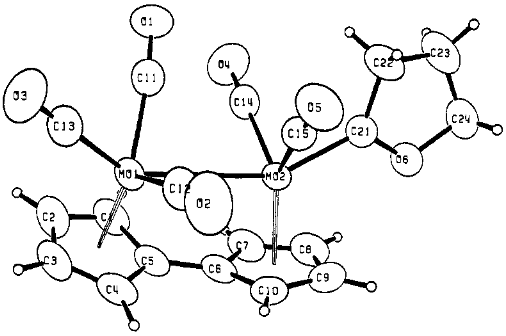


Figure 1. ORTEP drawing of **3**. Ellipsoids are scaled to represent a 50% probability surface.

We originally desired to prepare the trimethylene and fulvalene[3] bridged dimolybdenum derivative 2 as a more rigid analogue of other metal–metal nonbonded complexes[1c,e] reported to thermally extrude hydrocarbons. However, when the yellow dianion 1[4,6] [generated from (η^5:η^5-$C_{10}H_8$)$(CO)_6Mo_2$[3a,4] by treatment with 2.5 equiv of $LiBEt_3H$[5] in THF at 0–25 °C] was exposed to diiodopropane (1.5 equiv, 25 °C, 5 h) the red Fischer-type carbene 3 was formed[6] instead of 2 (Scheme II). In contrast, methylation gave the dimethyldimolybdenum derivative 4[4] (79%, mp 181–182 °C dec). An X-ray structural analysis of 3 (Figure 1) revealed an envelope-shaped 1-oxacyclopent-2-ylidene ligand, nearly coplanar with the

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† This paper is dedicated to the memory of my colleague and teacher, Professor E. L. Muetterties.

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[6] **1**: ^1H NMR (300 MHz, THF-d_8) δ 5.21 (m, 4 H), 4.76 (m, 4 H); IR (THF) ν_{CO} 1900, 1806, 1782, 1716 cm^{-1}. **3**: red crystals, 90%; mp 202–203 °C; MS, *m/e* (relative intensity) 530 (M^+, 4), 502 (9), 474 (1), 446 (13), 418 (6), 390 (18), 362 (3), 43 (100); ^1H NMR (200 MHz, acetone-d_6) δ 5.66 (m, 2 H), 5.40 (m, 2 H), 4.80 (m, 2 H), 4.74 (t, 2 H, J = 7.2 Hz), 4.52 (m, 2 H), 3.68 (t, 2 H, J = 7.6 Hz), 2.07 (tt, 2 H, J = 7.6, 7.2 Hz); ^{13}C NMR (45 MHz, C_6D_6) δ 231.6, 97.4, 94.0, 89.4, 85.9, 85.5, 83.3, 80.0, 56.2, 23.1; IR (KBr) ν_{CO} 1981, 1916, 1905, 1884, 1849 cm^{-1}. Anal. Calcd for $C_{19}H_{14}Mo_2O_6$: C, 43.04; H, 2.66. Found: C, 43.73; H, 2.84. X-ray, crystal size 0.10 × 0.22 × 0.32 mm; triclinic; space group $P\bar{1}$; a = 8.2680 (12) Å, b = 9.4957 (10) Å, c = 12.5989 (10) Å, α = 110.290 (7)°, β = 93.937 (9)°, γ = 92.049 (10)°; V = 923.7 (4) Å^3 at 25 °C; Z = 2; μ_{calcd} = 13.57 cm^{-1}; d_{calcd} = 1.906 g cm^{-3}; radiation = monochromatized Mo Kα ($\bar{\lambda}$ = 0.710 73 Å); scan range 3.0° ≤ 2θ ≤ 45°; reflections collected = 2411 unique, 2263 with $F^2 > 3\sigma(F^2)$, R = 1.77%, R_w = 3.27%.

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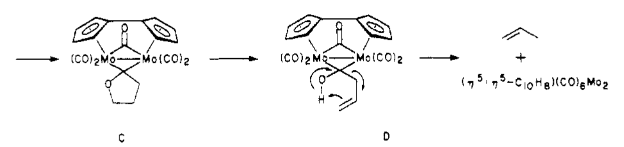
Scheme III



Mo–Mo bond, and the carbonyl groups slightly staggered to relieve steric compression, resulting in a twisted fulvalene. The generation of such carbene complexes from 1,3-dihalopropanes and nucleophilic metals has been observed previously[7] and mechanistically discussed in terms of addition of a nucleophile (which can be another metal) to a (γ-haloacyl)metal species generating a metallaenolate $R(CO)M^-$, capable of ring closure. However, the intermediacy of a dimetallacycle of the type **2** in those cases involving bimetallic systems has not been ruled out.

Complex **3** has two hitherto unobserved features. First, it is fluxional on the NMR time scale. Thus, on heating in toluene-d_8 the fulvalene signals begin to broaden while the oxopentylidene absorptions remain sharp. Because of the thermal instability of **3** (vide infra), quantification of these dynamics was only possible by using spin saturation transfer techniques.[8] This experiment revealed the exchange (50% magnetization transfer at 25 °C) between the respective sets of α and β protons on the fulvalene and also confirmed the absence of equilibration of the trimethylene hydrogens: $\Delta G^\ddagger = 18.0 \pm 0.5$ kcal mol^{-1}. The most appealing mechanism for this dynamic behavior would involve the intermediacy of a bridging carbene (Scheme III). Isomerizations of a bridging carbene to terminal positions have recently been observed,[1b,9] but not the reverse, and, although postulated,[7b] never directly in a Fischer-type carbene.[10]

Second, and most surprising, **3** on heating to 100 °C (benzene, $t_{1/2} = 12$ h) (or on irradiation) efficiently decomposes to regenerate $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(CO)_6Mo_2$ (80%) and propene (80%)! Deuterium-labeled **3**-d_2 at carbon-3[11] gave cleanly propene-*1,1*-d_2 (NMR, m/e), **3**-d_2 labeled at carbon-4[12] furnished propene-*2,3*-d_2, and **3**-d_1 labeled at carbon-5 through a novel sequence[13] resulted in propene-*3*-d_1. Recovered starting materials from incomplete thermolyses exhibited no label scrambling. These data rule out **2**, or any related dimetallacyclopentane, as being an intermediate in this reaction. Finally, there are no noticeable deuterium isotope effects (error margin ±10%), concentration dependence, and changes due to added ligand [such as $(C_6H_5)_3P$]. Remarkably, other oxacyclopentylidenes do not yield propene on pyrolysis but rather carbene dimers or 2,3-dihydrofuran.[10,14] The free carbene also furnishes the latter, but, in addition, cyclobutanone, cyclopropane, and ethylene,[15] not found in our system.

Scheme III depicts a possible mechanistic rationale for the observed data. It is appealing (but not required) to postulate that it is the relatively ready accessibility of the bridged carbene C (possibly facilitated[16,17] by the relatively electron-donating fulvalene ligand) which allows the unraveling of the ligand to D, much like a γ-butyrolactone pyrolysis,[18] followed by a retroene reaction, such as that observed with β,γ-unsaturated acids,[19] to furnish the products. This explains the absence of similar decomposition pathways in the related $Mn_2(CO)_{10}(CH_2)_3$,[14] as well as the mononuclear systems,[7,10,14] the outcome of the deuterium labeling experiments, and the other data. Whatever the exact mechanism, it is intriguing to speculate on the potential intermediacy of the hitherto unrecognized species of the type C and/or D or their unbridged counterparts in other propene-forming reactions involving dinuclear metallacycles and even on surfaces exposed to CO and H_2.

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Supplementary Material Available: A listing of positional and thermal parameters and tables of bond lengths and bond and torsional angles of **3** (11 pages). Ordering information is given on any current masthead page.

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[12] From $ICH_2CD_2CH_2I$ as in Scheme I.

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Reactions of a Methyl(methoxymethyl)rhodium(III) Complex. α-C–H and C–O Bond Cleavage and C–C Bond Formation[†]

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Summary: The complex $RhBr(CH_3)(CH_2OCH_3)(P(CH_3)_3)_3$ undergoes two different categories of reactions. If the C–O bond is cleaved, ethylene is formed by methyl group migration; if the Rh–Br bond is cleaved, methyl vinyl ether

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[†] Contribution No. 3585.

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